

## ***n*-GaN surface treatments for metal contacts studied via x-ray photoemission spectroscopy**

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The surface chemistry and electronic properties of *n*-GaN surfaces were studied via x-ray photoemission spectroscopy before and after wet chemical treatments. Shifts of the surface Fermi level were measured with the change in position of the Ga 3*d* core level peak. HCl treatment of *n*-GaN led to a 0.9 eV shift of the surface Fermi level toward the conduction band minimum, while KOH treatment led to a 0.3 eV shift of the surface Fermi level toward the valance band maximum. These shifts lead to a reduction in the surface barrier for HCl-treated *n*-GaN and for KOH-treated *p*-GaN, potentially improving contact resistance. The changes in surface chemistry indicate that a N (or Ga) deficiency with HCl(KOH) treatment alters the surface state density through the formation of donor (acceptor)-like states. © 2002 American Institute of Physics. [DOI: 10.1063/1.1430024]

GaN and related materials continue to grow in importance for optical and electronic devices.<sup>1</sup> A challenge in implementing these materials, due in part to their wide band gaps, is the formation of low resistance, ohmic contacts. While much literature has been published about contacts to *n*-type GaN, low resistance contacts to *p*-GaN have been difficult to achieve.<sup>2</sup> Due to the difficulty in forming contacts to *p*-GaN, a variety of contact techniques have been applied. Chemical treatments of the surface prior to any metal deposition have been used to reduce the contact resistance.<sup>3,4</sup> Previously, we reported on the surface chemistry and electronic properties of HCl- and KOH-treated *p*-GaN samples.<sup>5</sup> For *p*-GaN it was found that the HCl treatment led to an increase in the Ga/N ratio (Table I) which corresponded to a higher relative surface barrier height. Conversely, KOH treatment decreases the Ga/N ratio, which corresponded to a lower relative surface barrier height. These results agree with the previous articles for *p*-GaN which show that the HCl treatment prior to Pd deposition was sufficient to form a Schottky diode where the KOH treatment enabled the formation of an ohmic contact.<sup>3,4</sup> Here, HCl and KOH treatments on *n*-GaN are investigated to correlate changes in surface chemistry with changes in Fermi level position and hence contact resistance. In this study, we use synchrotron-based x-ray photoelectron spectroscopy (XPS) to both determine the chemical state of the sample surface as well as to monitor movement of the Fermi level.

The *n*-GaN samples were grown using metalorganic chemical vapor deposition on *c*-plane sapphire with a 20 nm GaN buffer layer followed by 1–2 μm *n*-GaN. The carrier concentration at the sample surface is 10<sup>16</sup>–10<sup>17</sup> cm<sup>-3</sup>, as determined by capacitance–voltage measurements. Samples that have not undergone any surface chemical treatment after

removal from the reactor will be referred to as the untreated samples. Some samples were immersed for 20 s in a boiling solution of KOH (~24 M). These samples were then rinsed in distilled water and dried in flowing N<sub>2</sub> and will be referred to as the KOH-treated samples. Additional samples, the HCl-treated samples, were immersed for 15 min in a solution of HCl (~6 M) and dried. The sample chemical treatments were done immediately prior to the introduction of the samples into the ultra-high vacuum analysis chamber. After analysis at room temperature, the HCl-treated samples were subsequently annealed *in situ* at 100 °C for 10 min. The XPS measurements were repeated after the sample cooled, and the sample was annealed in 100 °C increments for 10 min time periods, with measurements collected at room temperature between each anneal. XPS measurements were carried out at the University of Wisconsin's Synchrotron Radiation Center. The chamber is equipped with a double pass cylindrical mirror energy analyzer and attached to the Mark II beamline. The kinetic energy spectra were calibrated using the work function of the system, which was measured with the Fermi level of a grounded Ta foil, cleaned using annealing and argon ion sputtering.

The Ga 3*d*, N 1*s*, Cl 2*p*, and O 1*s* core levels, were monitored in each sample. As is commonly done, the movement of the surface Fermi level within the band gap was tracked by the shift of a core level, in this case the Ga 3*d*

TABLE I. Relative surface Ga-to-N ratio of various surfaces with the as-received sample as a reference. The HCl treatment increases the Ga/N ratio on both types of samples, while the KOH treatment decreases the Ga/N ratio on both sample types.

		As-received	HCl-treated	KOH-treated
<i>n</i> -GaN	Ga/N ratio	1.0	3.0 ± 0.1 <sup>12</sup>	0.52 ± 0.26
<i>p</i> -GaN	Ga/N ratio	1.0	2.7 ± 0.1 <sup>5</sup>	0.4 ± 0.1 <sup>5</sup>

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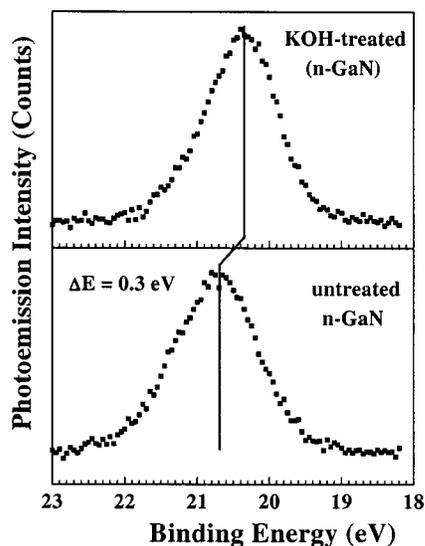


FIG. 1. Photoemission spectra of the Ga 3d core level on untreated *n*-GaN and a KOH-treated *n*-GaN sample. The lines indicate a shift of the Ga 3d peak by 0.3 eV toward the conduction band after the treatment. This does not favor lower contact resistance.

level.<sup>6</sup> The Ga 3d spectra, Fig. 1, were obtained for the KOH-treated and the untreated *n*-GaN. After the KOH treatment, the Ga 3d peak lies approximately 0.3 eV toward lower binding energy. This corresponds to a shift of the surface Fermi level 0.3 eV closer to the valence band maximum (VBM). A shift of the surface Fermi level in this direction indicates an increase of the surface band bending coincident with an increase of the surface barrier height on these samples. An increased surface barrier could result in an increased contact resistance.

For the HCl-treated samples, the shifts in the core levels were additionally determined after each stage of thermal annealing. For these samples, both the Ga 3d core level peak, as well as the Cl 2p core level peak, were monitored, as shown in Fig. 2. In Fig. 2(a), the thermal annealing of the HCl-treated sample gradually leads to a shift of the Ga 3d peak toward lower binding energy by about 0.9 eV. This shift is coincident with the removal of chlorinated species from the sample surface as seen by the disappearance of the Cl 2p core level peak in Fig. 2(b). The Cl 2p peak is undetectable after the 500 °C anneal. The presence of the chlorinated species on the surface is then correlated with a shift of the peak by about 0.9 eV toward higher binding energy. At first, one might suspect a chemical shift induced by Cl binding to Ga and shifting the Ga 3d peak to higher binding energy. Removal of Cl through annealing would then reverse the shift. However, in this case one would expect to see two separate Ga 3d peaks in Fig. 2(a), one for a Ga–Cl bond at the surface and one for the Ga–N bonds. During the anneal, the relative intensity of these two peaks would change with decreasing Cl coverage, but not their positions. In Fig. 2(a) we observe only one peak that shifts in a continuous fashion. That leads us to attribute the Ga 3d shift to a change in the Fermi level position within the band gap. If the chlorination with HCl leads to a shift of the peak toward higher binding energy, this corresponds to a shift of the surface Fermi level toward the surface conduction band minimum (CBM). A shift of the Fermi level in this direction indicates a decrease

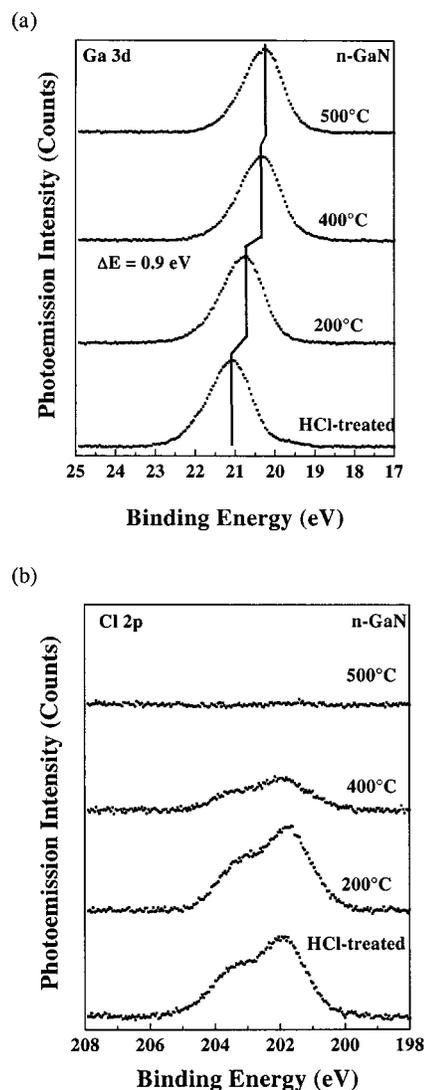


FIG. 2. (a) Photoemission spectra of the Ga 3d core level on the HCl-treated *n*-GaN sample after various temperature anneals. The lines indicate a shift of the Ga 3d peak by 0.9 eV toward the valence band with the chlorination. This favors lower contact resistance. (b) Photoemission spectra of the Cl 2p core level on the HCl-treated *n*-GaN sample after various temperature anneals. The Cl 2p peak is undetectable after the anneal to 500 °C, indicating the desorption of Cl-based species.

of the surface barrier height and surface band bending, which should lower resistance in contacts. Therefore, HCl treatment prior to metal deposition may lead to a lower contact resistance than KOH treatment on *n*-GaN. These results are consistent with electrical measurements in the literature.<sup>7–9</sup> Table II shows the previously determined surface barrier height on *n*-GaN surfaces treated with KOH or HCl. The barriers are determined by either *I*–*V* or *C*–*V*. The barrier height for the HCl-treated sample is consistently lower with either technique for Au or Ni Schottky diodes. The HCl does lead to a lower barrier height and will lead to a lower contact resistance. It is important to stress that the shifts reported are relative and are meant to compare the effectiveness of the two treatments. We have no way to measure the Fermi edge of the sample surface. Measurement conditions were chosen to minimize and to hold constant shifts due to nonequilibrium effects such as losses due to a “resistive” voltage drop at the sample contact as well as surface photovoltage

TABLE II. Surface barrier heights of Au and Ni Schottky diodes on KOH- and HCl-treated surfaces of *n*-GaN determined by *I*-*V* curves and *C*-*V* measurements.

	Au, $\Phi_b I-V$	Au, $\Phi_b C-V$	Ni, $\Phi_b I-V$	Ni, $\Phi_b C-V$
KOH treatment	1.03 <sup>8</sup>	1.03 <sup>8</sup>	1.15 <sup>8</sup>	1.11 <sup>8</sup>
HCl treatment	0.87 <sup>7</sup>	0.98 <sup>7</sup>	0.83 <sup>9</sup>	1.03 <sup>9</sup>

effects.<sup>10</sup> The relative shifts are therefore meaningful in the present study.

The N 1s core level was also measured, and the area of this peak as well as the area of the Ga 3d peak were used to determine a relative ratio of surface atomic concentrations. These ratios are relative, since they do not take into account the photoionization cross section or the transmission function of the spectrometer for each element. The ratios were therefore normalized to the ratio determined on the untreated sample, which becomes 1.0 for both *n* type and *p* type. The ratios are examined after the treatments to determine the relative changes in the surface chemical composition. These results are shown in Table I.<sup>11</sup> The HCl treatment leads to an increased Ga/N ratio due to the removal of a N-based species from the surface. This is consistent for both *n*- and *p*-GaN. Also, for both *n*- and *p*-GaN, the Ga/N ratio decreases on the KOH-treated samples. The removal of Ga from the surface, in this case, is most likely due to the formation and dissolution of Ga-based hydroxides.<sup>12,13</sup>

In the study of semiconductors there have been many models developed to explain Fermi level pinning behavior.<sup>14,15</sup> One of these models proposed by Spicer *et al.* describes Fermi level motion as being attributed to two bands of surface states, which correspond to Fermi level pinning positions associated with donor and acceptor character.<sup>16</sup> Changes in the surface stoichiometry can lead to the presence of only one of these types of surface states within the band gap and a corresponding shift in the surface Fermi level. It has been reported for GaN that N vacancies act as donors, while Ga vacancies act as acceptors.<sup>17-19</sup> Calculations have also shown that the N vacancies lead to a state near the conduction band minimum while the Ga vacancies lead to a state near the valence band maximum.<sup>20,21</sup> The increase of the Ga/N ratio after HCl treatment could correspond to the formation of N vacancies or similar N-related structural defects, resulting in the motion of the surface Fermi level toward the CBM. This is, again, consistent with previous observations of *p*-GaN with the shift toward higher binding energy leading to an increased surface barrier height on *p*-GaN. For the KOH treatment, the decrease in the surface Ga/N ratio could similarly correspond to Ga vacancies or related defects producing acceptors states with resulting motion of the surface Fermi level toward the VBM. Again, consistent results for *p*-GaN were previously observed, with a decrease in the surface barrier height, whereas in *n*-GaN there is an increase.

HCl treatment on GaN leads to an increase in Ga/N relative ratio due to the creation of N vacancies or related defects. These changes cause a decrease in band bending on *n*-GaN, making it a desirable treatment prior to metal deposition to potentially reduce the contact resistance. Addition-

ally, KOH treatment leads to a decrease in the Ga/N relative ratio due to the creation of defects such as Ga vacancies. These changes cause a decrease in band bending on *p*-GaN making it a desirable treatment prior to metal deposition due to the potential to decrease the contact resistance. With this knowledge of the effects HCl and KOH treatments have on the surface states and position of the surface Fermi level, new processes can be designed for minimizing contact resistance to *n*- and *p*-GaN materials. These processes would include HCl treatment for *n*-GaN or another treatment that would induce N vacancies; while KOH treatment, or another Ga vacancy-inducing treatment, would be used on *p*-GaN to ensure lower contact resistivity during contact formation.

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<sup>1</sup>S. Nakamura, *The Blue Laser Diode: The Complete Story* (Springer, Berlin, 2000).

<sup>2</sup>Q. Z. Liu and S. S. Lau, *Solid-State Electron.* **42**, 677 (1998).

<sup>3</sup>J.-L. Lee and J. K. Kim, *J. Electrochem. Soc.* **147**, 2297 (2000).

<sup>4</sup>J.-L. Lee, J. K. Kim, J. W. Lee, Y. J. Park, and T. Kim, *Solid-State Electron.* **43**, 435 (1999).

<sup>5</sup>J. Sun, K. A. Rickert, J. M. Redwing, A. B. Ellis, F. J. Himpsel, and T. F. Kuech, *Appl. Phys. Lett.* **76**, 415 (2000).

<sup>6</sup>G. Landgren, R. Ludeke, Y. Jugnet, J. F. Morar, and F. J. Himpsel, *J. Vac. Sci. Technol. B* **2**, 351 (1984).

<sup>7</sup>A. T. Ping, A. C. Schmitz, M. Asif Khan, and I. Adesida, *Electron. Lett.* **32**, 68 (1996).

<sup>8</sup>E. V. Kalinina, N. I. Kuznetsov, V. A. Dmitriev, K. G. Irvine, and C. H. Carter, Jr., *J. Electron. Mater.* **25**, 831 (1996).

<sup>9</sup>Q. Z. Liu, L. S. Yu, F. Deng, S. S. Lau, and J. M. Redwing, *J. Appl. Phys.* **84**, 881 (1998).

<sup>10</sup>F. J. Himpsel, *Surf. Sci. Rep.* **12**, 1 (1990).

<sup>11</sup>J. Sun, Ph.D. thesis, University of Wisconsin-Madison, 2000.

<sup>12</sup>*Gmelin Handbook on Inorganic and Organometallic Chemistry*, edited by H. Katscher and B. Mohsin (Springer, Berlin, 1996), Vol. C2.

<sup>13</sup>J. L. Weyher, S. Müller, I. Grzegory, and S. Porowski, *J. Cryst. Growth* **182**, 17 (1997).

<sup>14</sup>W. Mönch, *Semiconductor Surfaces and Interfaces*, 2nd ed. (Springer, Berlin, 1993), Vol. 26.

<sup>15</sup>F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces: Their Atomic and Electronic Structures* (Academie, Berlin, 1988).

<sup>16</sup>W. E. Spicer, Z. Liliental-Weber, E. Weber, N. Newman, T. Kendelewicz, R. Cao, C. McCants, P. Mahowald, K. Miyano, and I. Lindau, *J. Vac. Sci. Technol. B* **6**, 1245 (1988).

<sup>17</sup>D. C. Look, D. C. Reynolds, J. W. Hemsky, J. R. Sizelove, R. L. Jones, and R. J. Molnar, *Phys. Rev. Lett.* **79**, 2273 (1997).

<sup>18</sup>K. Saarinen, T. Laine, S. Kuisma, J. Nissilä, P. Hautojärvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wyszomolek, T. Suski, M. Leszczynski, I. Grzegory, and S. Porowski, *Phys. Rev. Lett.* **79**, 3030 (1997).

<sup>19</sup>D. E. Boucher, Z. A. Gál, G. G. DeLeo, and W. B. Fowler, *Mater. Res. Soc. Symp. Proc.* **482**, 941 (1998).

<sup>20</sup>J. Neugebauer and C. G. Van de Walle, *Phys. Rev. B* **50**, 8067 (1994).

<sup>21</sup>J. Neugebauer and C. G. Van de Walle, *Mater. Res. Soc. Symp. Proc.* **339**, 687 (1994).